SCIENCE FOR CERAMIC PRODUCTION

DEFECTS IN BERYLLIUM CERAMICS

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Point defects and possible reasons for defect formation in beryllium ceramics with B^{3+}, Al^{3+}, Zn^{2+}, Li^+, and rare-earth element impurities produced by slip casting, dry-press molding, and high-temperature compression are investigated using electron paramagnetic resonance. A certain number of impurity centers are identified which determine the optical, luminescent, diffusion, and other physicochemical properties of beryllium ceramics.

Ceramics based on beryllium oxide have unique physicochemical properties, including high chemical, thermal, dielectric, and radiation resistance and heat conductivity. Beryllium oxide is a wide-ranged dielectric material (with a prohibited zone width of ≈ 10.7 eV) and is permeable to x-ray and microwave radiation. Articles made of beryllium ceramics are currently widely used as refractories, heat-removal insulators, transistor and microcircuit substrates, microwave windows and insulators, dielectric discharge tubes in resonators and waveguides in gas lasers, working agents in ionizing radiation sensors, neutron reflectors, etc.

In connection with their wide area of application, the study of inherent and impurity defects in beryllium ceramics is of great significance. The mechanism of the emergence and interaction of defects in BeO remains to a large extent unknown. Beryllium ceramics compared to BeO single crystals have a higher content of impurities, which are sources of defects and have a substantial effect on the properties of ceramics.

Several types of point defects in the anion and cation sublattices of BeO were identified using the electron paramagnetic resonance method (EPR) [1, 2]:

F^+ center (an anion vacancy that has captured one electron);

F^0 center (an anion vacancy that has captured two electrons);

V^- center (a cation vacancy that has captured one hole);

V^+ center (a cation vacancy that has captured two holes).

The prevailing type of impurity defects are B^{3+}, Al^{3+}, Zn^{2+}, Mg^{2+}, and Li^+, which isomorphically replace Be^{2+} ions in the cation sublattice. Beryllium oxide differs from other oxides by a relatively low isomorphic impurity capacity ($10^{-4} - 10^{-3}$ wt.%). Part of the impurities in ceramics which quantitatively exceed the isomorphic capacity in BeO crystal lattice are located on the faces of microcrystals and pores, thus forming surface microstructures. One should discriminate the impurities penetrating into beryllium ceramics from the initial BeO powder and the impurities deliberately introduced into the ceramic composition in order to impart additional physicochemical properties to ceramic materials.

The formation of point defects in beryllium hydroxide powders (BH) and basic beryllium carbonate (BBC) in the course of their technological processing and production of BeO powder used in ceramic manufacture is studied in [3]. It is shown that two types of paramagnetic centers are present in BeO powders: hole centers V^- and electron centers F^+ with the following spectroscopic parameters: $g_1 = 2.012$, $\Delta H = 8$ G, $g_2 = 2.004 \pm 0.005$, $\Delta H = 13$ G, and $g_3 = 1.989$, $\Delta H = 5$ G. The signal corresponding to the F_s^+ center is the most typical of BeO powder produced by decomposition of initial BH and BBC in air or in vacuum at a temperature not exceeding 770 K. In this case a highly defective structure of BeO is formed. This signal totally disappears after heat treatment of powder at a temperature above 1740 K. Heat treatment of powders usually intensifies the hole signal corresponding to the V^- center. The formation of point defects in BeO powder depending on the heat-treatment conditions can be represented by the quasichemical reactions inside the volume

$$Be^{2+} + O^{2-} = Be^{2+} + F^+ + e^- + 1/2O_2$$
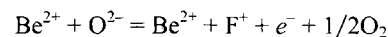
and on the surface of the powder

$$Be^{2+} + O^{2-} = Be^{2+} + F_s^+ + e^- + 1/2O_2.$$
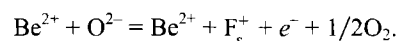
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Similar EPR results were obtained for BeO powder after thermal-vacuum decomposition of BH. In this case the EPR signals registered at temperatures of 300 and 77 K were typical of the V^- center with $g_1 = 2.001 \pm 0.95$, $\Delta H = 12$ G and $g_2 = 2.001 \pm 0.005$, $\Delta H = 20$ G and the intense surface F_s^+ center with $g_3 = 1.988 \pm 0.05$ and $\Delta H = 30$ G.

Apart from the inherent defects, impurity defects of Fe^{3+} ions were identified in BeO powder and ceramics using the EPR and the optical absorption methods, and these defects have a significant effect on the microstructure of beryllium ceramics [4, 5]. As follows from the chemical analysis of BeO powder used in ceramic production, the weight content of iron impurities in the powder varies in the range of $(0.07 - 0.57) \times 10^{-1}$%. In sintering of beryllium ceramics produced by the traditional technology (dry-press molding or slip casting) at a temperature of 2220 K, iron impurities have a substantial effect on the heterogeneity of the granular microstructure of ceramics and produce areas tinted in gray and dark colors. It was found that these zones are characterized by significantly larger (twice as large or more) sizes of microcrystals, compared to their average size in the white-colored area. In order to clarify the role of iron in the formation of the disperse ceramic structure, white and tinted areas of ceramics were investigated using the EPR method. Some ceramic samples were irradiated by a Mikrotron M-20 accelerator using characteristic x-ray radiation with effective and boundary energies $E_{ef} = 4.5$ MeV and $E_b = 12$ MeV. The exposure dose was 1500 R. The EPR parameters of Fe^{3+} ions in beryllium ceramics are shown in Table 1.

A wide EPR signal with the spin-Hamiltonian parameters $g = 2.8$ and $\Delta H = 2500$ G typical of Fe^{3+} ions was identified in the samples with a dark-gray tint and a large average grain size (40 – 80 μm). A weaker signal was registered in the non-radiated samples at a temperature of 153 K. At 77 K this signal became much wider. The light-gray samples with a grain size within the range of 15 – 40 μm at room temperature exhibited an EPR signal with $g = 2.17$ and $\Delta H = 740$ G. As the temperature decreased to 153 K, the signal became wider with $g = 2.19$ and $\Delta H = 800$ G. At a temperature of 77 K the signal became still wider ($g = 2.24$ and $\Delta H = 950$ G).

Radiation of these very samples caused the emergence of relatively weak EPR signals at room temperature (1.5 – 2 times smaller amplitude than before the radiation) with $g = 2.09$ and $\Delta H = 500$ G. Chilling to 153 K caused an increase in the g-factor to 2.12 and the ΔH field to 740 G. Radiation of the tinted samples was accompanied by the conversion of part of the Fe^{3+} and Fe^{2+} ions, which are registered by the EPR method only at helium temperatures. Fe^{2+} ions do not tint beryllium ceramics in the visible spectrum range. In the white samples the EPR signal typical of Fe^{3+} was absent or weak.

Thus, industrially manufactured ceramic articles made of BeO emit two types of signals typical of Fe^{3+} ions, which differ significantly in their spectroscopic parameters. The signal with $g = 2.800 \pm 0.005$ and $\Delta H = 250$ G is probably caused by Fe^{3+} ions in the surface and near-surface (at the interface of BeO microcrystals and pores) formations and $Fe^{3+} - O - Fe^{2+}$ clusters, in which the exchange between iron ions is very intense. This is indicated by the presence of a wide optical absorption band in the violet range of the spectrum with an absorption maximum of 430 nm (34,492 cm^{-1}) and a wide EPR signal ($\Delta H \approx 2500$ G). The second signal with $g = 2.170 \pm 0.005$ and $\Delta H = 750$ G can be associated with the presence of iron ions in the near-surface layer of BeO microcrystals and, possibly, partial incorporation of Fe^{3+} crystals in the BeO crystal lattice or formation of $Fe^{3+} - O - Fe^{3+}$ clusters, in which the exchange between $Fe^{3+} - Fe^{3+}$ ions is less intense.

The analysis of dark-colored Al_2O_3 ceramics using the EPR method revealed the presence of a wide signal corresponding to Fe^{3+} ions at a temperature of 300 K ($g = 2.170 \pm 0.005$ and $\Delta H = 680$ G). At 77 K the signal became much wider and had the following parameters: $g = 2.220 \pm 0.005$ and $\Delta H = 970$ G. After service of the articles for 100 h at 1470 K, no EPR signal of Fe^{3+} was identified. Thus, iron ions in the tinted samples of BeO and Al_2O_3 ceramics have similar EPR signals probably caused by the formation of iron ion clusters with a similar structure.

Particular attention should be paid to defects in transparent beryllium ceramics produced by high-temperature compression of BeO powder in vacuum at temperatures around 1550 K according to the method described in [6]. Lithium, B_2O_3, and rare-earth impurities were introduced into the powder before compression. Iron impurities were present in the initial powder. The optical analysis showed that samples that were not subjected to ionizing radiation exhibited a wide charge-transfer band with a maximum at 430 – 450 nm and several narrow bands in the UV range with maxima at 135, 245, and 290 nm related to the presence of iron impurities in the form of clusters in the ceramics. In certain thermodynamic conditions when beryllium ceramics is sintered or compressed in a relatively weak reducing medium (in graphite batch or tooling), Fe – O – Fe cluster chains of various lengths arise.

As the result of the study of EPR spectra of transparent beryllium ceramics after ionizing radiation, it was established that they consist of wide intense bands corresponding to Fe^{3+} ions. The band width and the values of the spectro-

TABLE 1

| State of sample	Temperature of EPR spectrum registration, K	g-factor	ΔH, G
Not irradiated, dark	300	2.80	~2500
Not irradiated:			
gray	300	2.17	740
gray	153	2.19	800
gray	77	2.24	950
After irradiation:			
gray	300	2.09	500
gray	153	2.12	740
gray	77	2.15	800

scopic splitting factors for hot-pressed beryllium ceramics at 300 K are given in Table 2.

The wide signals with g-factors in the range of $2.047 - 2.400$ and $\Delta H = 188.4 - 841.6$ G in transparent samples of beryllium ceramics belong to Fe^{3+} ions which are part of $Fe^{3+} - O - Fe^{3+}$ clusters of different sizes. The great spread in the spectroscopic parameters is probably related to the quantity of iron impurities in the initial BeO powder, as well as the structural specifics of clusters and the production technology of the beryllium ceramics.

Synchrotron radiation of samples on a VEPP integrator using a dose of 10 R (with a photon energy of $3 - 62$ keV) produced the emergence of relatively intense EPR signals with $g = 1.992$ and $\Delta H = 8.1$ G, which are probably inherent in the F^+ center. This center is stable at room temperature and manifests itself only after radiation. It is known [7] that F^+ centers emerge in BeO single crystals either after radiation by fast neutrons with a fluence of 5×10^{16} cm^{-2} or after isochronic roasting in metallic beryllium vapor (additive tinting).

Beryllium oxide belongs to the A^2B^6 class of compounds and has a structure of the wurtzite type; therefore, its crystallographic analogue, i.e., zinc oxide, is of a certain interest. An EPR signal of the F^+ center with similar parameters is registered in zinc oxide [8]. After introducing Li_2O at a temperature of 77 K, an EPR signal with $g = 1.957$ and $\Delta H = 9$ G was obtained. A deviation from stoichiometry in beryllium oxide, the same as in ZnO, is possible either due to the introduced beryllium or due to oxygen vacancies. The EPR signals registered by us in transparent beryllium ceramics are probably inherent in the F^+ center ($g = 1.992$ and $\Delta H = 8.1$). As can be seen from Table 2, the registered narrow signal from the electron centers with $g = 1.978$ and $\Delta H = 4.8$ G which are observed only in beryllium ceramic samples with 0.6 wt.% Li_2O additive can be attributed to the manifestation of a donor area produced by the substantial increase in the concentration of oxygen vacancies. It can be assumed that weak EPR signals in beryllium oxide with g-factors 1.987 and 1.978 are sent by the centers similar to the F_s-center and are determined by trapping of electrons at the defects near

TABLE 2

Chemical composition of samples, wt.%	G-factor (± 0.005)	ΔH, G
BeO + 3.0Li$_2$O	2.260	188.4
(without irradiation)	2.019	297.8
BeO + 0.05B$_2$O$_3$ + 0.42Li$_2$O	2.255	841.6
(without irradiation)		
BeO + 0.2B$_2$O$_3$ + 0.3Li$_2$O	2.074	827.3
(without irradiation)		
BeO + 0.01B$_2$O$_3$ + 0.42Li$_2$O	2.400	670.1
(irradiation by synchrotron)	1.992	8.1
	1.987	5.1
BeO + 0.6Li$_2$O	2.380	600.0
(irradiation by synchrotron)	1.992	8.1
	1.987	3.0
	1.978	4.8

the surface of BeO microcrystals. The insignificant width of these signals points to the weak interaction with the neighboring centers, which lack circular coordination. The scheme of formation of substitutional solid solutions BeO – Li$_2$O can be represented in the following form:

$$(BeO)_{1-x} + x(1/2Li_2O) \rightarrow Be_{1-x}Li_xO_{1-x/2} + x/2V_0.$$
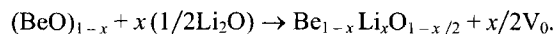
As the result of heterovalent substitution of Li$^+$ for Be$^+$, oxygen vacancies V_0 arise. Under the effect of radiation, conductivity electrons, which are F$^+$ centers that can be registered by the EPR method, are localized in them.

It was found by us [6, 9] that F$^+$ centers are capable of substantial modification of optical and luminescent properties of beryllium ceramics and increase the luminescent intensity compared to ceramics without the addition of lithium oxide.

As for boron impurities in beryllium ceramics, its introduction should be accompanied by the emergence of two types of EPR centers: a V$^-$ hole center, which is a beryllium vacancy with a trapped hole, and the electron center corresponding to B^{2+} ions which isomorphically replace Be^{2+} ions. The center's typical B^{2+} ions were not registered in transparent beryllium ceramics with B$_2$O$_3$ impurity, since EPR spectra in samples with and without boron impurities are totally identical.

It is likely that we obtained beryllium ceramics with additives of Ce^{3+} ions (without lithium oxide impurities) by impregnation with a metal melt containing metallic cerium [10] at a temperature of 2073 K in a helium atmosphere. The impregnation caused consolidation of ceramics and the formation of a grayish-yellow tint. The absorption and luminescence spectra of the obtained samples corresponded to allowed transitions $4f$-$5d$ in the Ce^{3+} ion. EPR signals were not registered in ceramics not subjected to ionizing radiation. X-ray radiation (dose of 600 R at 300 K) resulted in the emergence of three EPR signals with the following parameters: a weak signal with $g_1 = 2.021$ and $\Delta H = 15$ G, an intense one with $g_2 = 2.021$ and $\Delta H = 15$ G, and a signal with $g_3 = 1.987$ and $\Delta H = 30$ G.

Chilling of ceramic samples to helium temperature results in substantial widening of the signal and decrease in the duration of spin-lattice relaxation. The most intense signal with $g_1 = 2.201$ can be attributed to beryllium vacancies with localized holes. The weak signal with $g_2 = 2.091$ is hard to interpret.

Of special interest is the presence of a signal corresponding to the electron center with $g_3 = 1.987$. In our opinion, this is an F$^+$ center located in the near-surface zone of BeO microcrystals. Similar EPR signals were registered by us after heating BH or BBC samples to the temperature of their dehydration and decomposition. It was found [9] that impurities of rare-earth elements (REE) in small quantities isomorphically replace Be^{2+} ions in the cation sublattice, and the main part of the impurity is located on the surface of the BeO microcrystals and pores. REE impurities have a greater affinity to oxygen than beryllium has, which results in the formation of oxygen vacancies in the surface or near-surface

parts of the microcrystals, which are stable at room and increased temperatures [9]. Under the effect of ionizing radiation, a conduction electron is formed in the oxygen vacancy and an Fe^+ center emerges. It was shown in [6, 9] that simultaneous introduction of Li_2O and REE oxides is accompanied by increased luminescence of hot-molded transparent beryllium ceramic samples, which is several times greater than that of similar samples without the specified impurities.

Of great interest is the study of conducting beryllium ceramics with additives of 5 – 30 wt.% TiO_2 [11]. The electric conductance of such ceramic is significantly affected not only by the amount of additive but also by the sintering conditions and the atmosphere in the kiln. The sintering of ceramics was performed in forevacuum kilns with graphite heaters at a temperature not exceeding 1750 K. After sintering, the samples were additionally heat-treated in hydrogen. The electric resistance of samples obtained at a temperature of 300 K varied in the range of $6 \times 10^3 - 8 \times 108 \ \Omega \cdot cm$ depending on the quantity of the introduced TiO_2, whereas without TiO_2 additives it was $1 \times 10^{14} - 1 \times 10^{15} \ \Omega \cdot cm$.

The x-ray phase analysis of beryllium ceramics with TiO_2 additives showed that along with the rutile-phase impurities, the low-temperature anatase modification of Ti_2O was present as well in the ceramics, and being heated to 950 K, it should completely change over to rutile. This is the evidence of the fact that part of the beryllium ions are dissolved in TiO_2, as a consequence of which the low-temperature modification of TiO_2 is stabilized. After sintering at a temperature of around 1750 K and additional heat-treatment in hydrogen, ceramics with TiO_2 additives acquired a dark-gray color. The physicochemical properties of such ceramics are considered in detail in [11].

EPR spectra of beryllium ceramics with TiO_2 impurity were obtained in the x-spectrum on x-radiated and non-x-radiated samples. Immediately after sintering and hydrogen treatment at temperature of 1370 K (1.5 h), samples at 77 K exhibited EPR signals with $g = 1.930 \pm 0.005$ and $\Delta H = 170$ G. The radiation caused a slight narrowing of the signal to $\Delta H = 15$ G, whereas the value of the g-factor virtually did not change. Apart from the electron center corresponding to Ti^{3+} ions, a weak hole signal with $g = 2.018 \pm 0.005$ and $\Delta H = 5$ G was registered only in the radiated samples. The radiation also resulted in some narrowing of the EPR signal and a decrease in its intensity. Heating of ceramic samples to 50 – 60 K above the nitrogen boiling temperature was accompanied by a sharp change in the paramagnetic center relaxation time and disappearance of the EPR signal. Additional heat treatment of ceramics in air at 1670 K increased the width of the signal of Ti^{3+} ions up to $\Delta H = 180$ G. After radiation, an intense hole signal with $g = 2.016 \pm 0.005$ and $\Delta H = 10$ G was registered.

It is known [12] that paramagnetic centers created by Ti^{3+} ions in the crystals of beryl $Be_3Al_2Si_6O_{18}$ at a temperature of 77 K are characterized by a signal with $g = 1.997 \pm 0.005$ and $\Delta H = 22.3 \pm 0.7$ G and a narrow EPR band. EPR spectra for Ti^{3+} ions located in the octahedral environment are usually observed at helium temperatures, since the main term ^2D

in this case is orbitally thrice degenerated, which is characterized by a great width of the EPR band at the usual temperatures as well as a short relaxation time. The defects distorting the octahedron crystal field reduce degeneration and result in narrowing of the spectrum.

The wide and intense EPR signals from Ti^{3+} ions at a temperature of 77 K are probably associated with the emergence of clusters of the $Ti^{3+} - O^{2-} - Ti^{3+}$ type on the surface of BeO microcrystals. Inside these clusters Ti^{3+} ions exchange intensely. Since the low-temperature phase of TiO_2 (anatase) is stabilized in sintering, Be^{2+} ions probably replace Ti^{4+} ions in oxygen octahedrons, although such substitution is not typical of beryllium ions.

Thus, beryllium oxide is extremely sensitive to the impurity phase. The main inherent point defects identified by the EPR method in BeO powder and ceramics are V^- and F^+ centers. Apart from the inherent defects, a certain amount of impurity centers which determine the optical, luminescent, diffusion, and other physicochemical properties of ceramics have been identified in beryllium ceramics produced by various methods (slip casting, dry-press molding, high-temperature compression).

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